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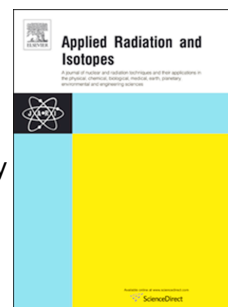
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Theory and Experiment of Optical Absorption of Platinum Nanoparticles Synthesized by Gamma Radiation

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Abstract:

Platinum nanoparticles were synthesized using the gamma radiolytic technique in an aqueous solution containing Platinum tetraammine chloride in presence of poly vinyl pyrrolidone, isopropanol, tetrahydrofuran and deionised water. The gamma irradiation was carried out in a ⁶⁰Co gamma source chamber and the particle size was found to decrease from 4.88 to 3.14 nm on increasing the gamma radiation dose from 80 to 120 kGy. UV-visible absorption spectra were measured and revealed two steady absorption maxima at 216 and 264 nm in the UV region, which was blue shifted (i.e. toward lower wavelength) with decreasing particle size. By taking the conduction electrons of an isolated particle that are not entirely free, but instead bound to their respective quantum levels, the optical absorption of platinum nanoparticles can be calculated via intra-band quantum excitation for particle sizes similar to those measured experimentally. We found that the calculated absorption maxima of electronic excitations matched the measured absorption maxima well. This finding suggests that the optical absorption of metal nanoparticles commonly applied in nanoscience and nanotechnology can be described accurately by the quantum excitation of conduction electrons.

Keywords: Platinum nanoparticles; gamma radiolysis; optical absorption; absorption maxima; intra-band quantum excitation; theory of metal nanoparticles.

1. Introduction

The development of nanoscience and nanotechnology opens up novel prospects of metal nanoparticles for applications in many fields, particularly in catalysis. The unique physical and chemical properties of nanoparticles, which are distinctive from their bulk counterparts, have great potential for chemical and biological sensing (Kang et al., 2008).

Colloidal metal nanoparticles have attracted great attention in the field of catalysis due to their considerable catalytic activity (Jia and Schüth, 2011; Tao, 2014) and also played a significant role in the electronic and optical properties (Zaniewski et al., 2013). Scientists investigated the colloidal metal nanoparticles catalysts in various reactions in homogeneous catalysis including hydrogen peroxide decomposition (Jia and Schüth, 2011; Klabunde and Richards, 2001) and hydrazine in aqueous solution (Klabunde and Richards, 2001). For instance, colloidal platinum nanoparticles, generally participate in hydrogenation reactions to expedite the procedures (Lewis and Lewis, 1986).

Platinum (Pt) is one of the important metals in catalysis and, as nanoparticles, they have been extensively used for numerous applications, including gas sensors (Chen and Holt-Hindle, 2010; Kang and Kim, 1993), glucose sensors (Zhai et al., 2013), and catalysts in fuel cells (Antolini, 2007; Chen and Holt-Hindle, 2010; Krishnamurthy and Deepalochani, 2009; Long et al., 2011a) and in car exhaust systems (Chen and Holt-Hindle, 2010; Hoshika et al., 2010). However, the principle mechanism of catalytic action by metallic nanoparticles has not yet been established, partly because the classical interpretation of metal nanoparticles under influenced of electric field oscillation does not allow conduction electrons from leaving the particle to interact with the surrounding medium. The sensitivity of metal nanoparticles in chemical and biological sensing is somewhat related to the action of conduction electrons interacting with the surrounding chemical and biological entities. In this spirit, a better description of metal nanoparticles is required, in order to understand catalytic action by metallic nanoparticles.

The properties of Pt nanoparticles are influenced by particle size, shape, and structure, which can be controlled through the manufacturing procedure. There are numerous reports of the synthesis of Pt nanoparticles. Various techniques for the manufacture of colloidal Pt nanoparticles are the chemical reduction approach (Chen and Akashi, 1997; Li et al., 2009; Long et al., 2010), the

polyol process (Mizukoshi et al., 2001), the two-phase liquid-liquid route (Castro et al., 2009), microemulsions (Ingelsten et al., 2001), green synthesis (Coccia et al., 2012), and gamma irradiation (Wang et al., 2006). Among the different techniques, the gamma irradiation method presents the several benefits. One of the important advantages of the gamma irradiation synthesis in comparison with the other available methods lies in the fact that the main reducing agent in the absence of oxygen is the hydrated electron which has a very negative redox potential. This enables any metal ions to be reduced to zerovalent metal atoms without using chemical reducing agents. Therefore, the generation of primary atoms occurs as an independent event and at the origin; the atoms are separated and homogeneously distributed as were the ionic precursors (Abedini et al., 2013; Belloni, 1996; Henglein, 1993, 1995). In other words, two main factors which lead to formation of uniformly dispersed and highly stable nanoparticles without unwanted by-products of the reductants are homogeneous formation of nuclei and elimination of excessive chemical reducing agents (Abedini et al., 2013). For instance, the formation of Ag nanoparticles by gamma radiolytic method divided into two steps including the formation of the Ag atoms by the nucleation process and the formation of Ag nanoparticles by the aggregation process (Saion et al., 2013). Hence, the radiation-induced synthesis of metal nanoparticles, especially Pt nanoparticles are very important.

The optical properties of metal nanoparticles have long been of interest in physical chemistry, starting with Faraday's investigations of colloidal gold (Kelly et al., 2003). The optical absorption of semiconductor nanoparticles is related to electronic structure in terms of an inter-band electronic excitation from the fully occupied valence band to the conduction band, depending on size and shape (Noguez, 2007). However, the optical absorption of metal nanoparticles is dominated via their localized surface plasmon resonances (LSPR) that are associated with the collective coherent oscillation of conduction electrons in resonance with the incident electromagnetic wave, which depends on the dielectric constants of the particles and the medium (Chen et al., 2011; Mie, 1908). Moreover, photocatalytic action of semiconductor nanoparticles is well defined, but the definition of catalytic action of metal nanoparticles is less obvious, although some transition metals can influence the photocatalytic activity (Liao et al., 2012). The oscillating conduction electrons of metallic nanoparticles cannot contribute to photocatalytic action because no electronic exchange can take place between the particles and the medium to initiate catalysis. Thus, searching for a new theory of metal nanoparticles is

fundamental for interpretation of the photocatalytic action and the mechanism of heterogeneous catalysis.

The optical absorption spectra of Pt nanoparticles remain obscure because of their characteristics. Previously, it was announced that chemically or electrochemically synthesized Pt nanoparticles display a single absorption peak in the UV spectrum in the region 252–259 nm (Long et al., 2011b). Pt nanoparticles showing two absorption peaks at about 220 and 260 nm have also been reported (Bragau et al., 2010; Henglein et al., 1995; Jiang et al., 2006; Liu and Jiang, 2006; Liu et al., 2006).

This article reports an experiment to synthesize colloidal Pt nanoparticles in the size range 3.14–4.88 nm, which was achieved via the gamma radiolytic technique, using a complex platinum salt as the metal precursor. Measurement of the optical absorption of the prepared particles was carried out and the absorption maxima were compared with calculated values via intra-band quantum excitation of conduction electrons of an isolated single Pt nanoparticle of similar size.

2. Experimental

2.1. Materials

Platinum tetraammine chloride hydrate, $(\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O})$ was used as the metal precursor, poly vinyl pyrrolidone (PVP) as the capping agent to lessen the agglomeration of Pt nanoparticles, isopropanol (IPA) as a scavenger of hydrogen and hydroxyl radicals, and tetrahydrofuran (THF) and deionized water as solvents for the metal complex and polymer, respectively. PVP (MW = 29000), IPA, and THF were acquired from Sigma–Aldrich. The precursor, capping agent, and radical scavenger were used without further purification.

2.2. Procedure

0.42 g of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ was dissolved in 50 mL of THF before introducing into an aqueous solution of 3 g PVP in 150 mL of deionized water. After adding 20 mL of IPA the mixture solution was magnetically stirred and bubbled with 99.5% nitrogen gas for 1 h before placing the solution into several glass tubes. The samples were irradiated with ^{60}Co gamma rays irradiation facility model (J. L. Shepherd) at the Malaysian Nuclear Agency at different doses of 80, 90, 100, 110, and 120 kGy.

The ^{60}Co produces two main gamma rays of 1.17 and 1.33 MeV which give the average energy of 1.25 MeV. The gamma facility was calibrated using Fricke dosimeter, and the dose rate was calculated based on the half-life ($T_{1/2}$) of the source, (i.e. the elapsed time in which the activity of the source reduced by half) according to the following equation:

$$\dot{D} = \dot{D}_0 \exp\left(-\ln \frac{2t}{T_{1/2}}\right) \quad (1)$$

where \dot{D}_0 is the dose rate (1.2 (kGy/h)) at time $t=0$.

2.3. Characterization

The optical absorption spectrum was acquired on a UV–visible spectrophotometer (UV-1650PCSHIMADZU). There was no treatment of the irradiated samples prior to the optical absorption analysis. The particle size and the size distribution were resolved using a HITACHI transmission electron microscope (TEM; H 7500), employing an accelerating voltage of 100 kV. The TEM samples were prepared by placing a drop of the irradiated solution on a copper grid and allowing the specimen to dry naturally overnight.

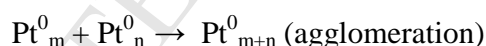
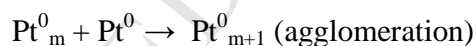
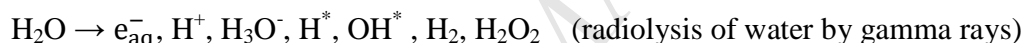
3. Results and Discussion

3.1 Formation of Pt nanoparticles

Platinum nanoparticles were prepared using the gamma irradiation method. Among the diverse traditional approaches, the gamma radiolytic technique presents a couple of benefits. It is an uncomplicated process that generates entirely reduced and considerably pure metal nanoparticles, which are free from other products or reducing agents (Eisa et al., 2011; Li et al., 2007; Naghavi et al., 2010; Saion et al., 2013; Soliman, 2014; Wang et al., 2006).

The fundamental interaction of gamma photons with matter includes various distinct processes, depending on the energy of the photons and the density and atomic number of the medium. 1.25-MeV ^{60}Co gamma rays interact with matter in aqueous solution by photoelectric absorption, Compton scattering, and pair production to form secondary electrons, which mainly arise from the Compton scattering.

The secondary electrons can induce reactive species, such as hydrated electrons (e_{aq}^-), hydroxyl radicals (OH^\bullet), and hydrogen radicals (H^\bullet) by radiolysis of water (Naghavi et al., 2010). Platinum tetraamminechloride in water dissociates into positive $[Pt(NH_3)_4]^{2+}$ ions and negative Cl^- ions. Furthermore, the hydrated electrons e_{aq}^- reduce $[Pt(NH_3)_4]^{2+}$ ions to zero valent Pt atoms (Pt^0) by the first nucleation process. Hydroxyl and hydrogen radicals (OH^\bullet and H^\bullet), induced in the radiolysis of water, are additionally strong reducing agents in aqueous colloidal solution. To prevent this, isopropanol (IPA) was added to the precursor solutions as radical scavengers of hydrogen and hydroxyl radicals (Naghavi et al., 2010; Saion et al., 2013). The H^\bullet and OH^\bullet radicals are scavenged by the IPA molecules, forming isopropanol radicals (IPA^\bullet), which subsequently reduce $[Pt(NH_3)_4]^{2+}$ ions into Pt^0 . Since no additional reducing agent is employed, the procedure of the creation of Pt^0 atoms by reduction of the Pt salt by hydrated electrons or by IPA radicals continues as long as the specimens are irradiated with gamma rays. Many Pt^0 atoms can agglomerate to form Pt_2^0 dimers or Pt_m^0 nanoparticles. Large Pt_m^0 nanoparticles can agglomerate further with other nanoparticles Pt_n^0 to form even larger Pt_{m+n}^0 nanoparticles.



3.2. Structural properties

The TEM images and size distributions of Pt nanoparticles generated by gamma doses of 80 kGy and 90 kGy are shown in Figure 1. The average particle sizes obtained by Gaussian fitting of the size histograms are 4.88 nm and 3.90 nm, respectively. Overall, the average particle sizes were found to be 4.88, 3.90, 3.56, 3.31, and 3.14 nm for doses of 80, 90, 100, 110, and 120 kGy, respectively. The reduction of nanoparticle size with increasing dose has been discussed elsewhere (Abedini et al., 2012): by increasing the dose, the particle size becomes smaller because the nucleation process increases faster than the aggregation process in the formation of Pt nanoparticles.

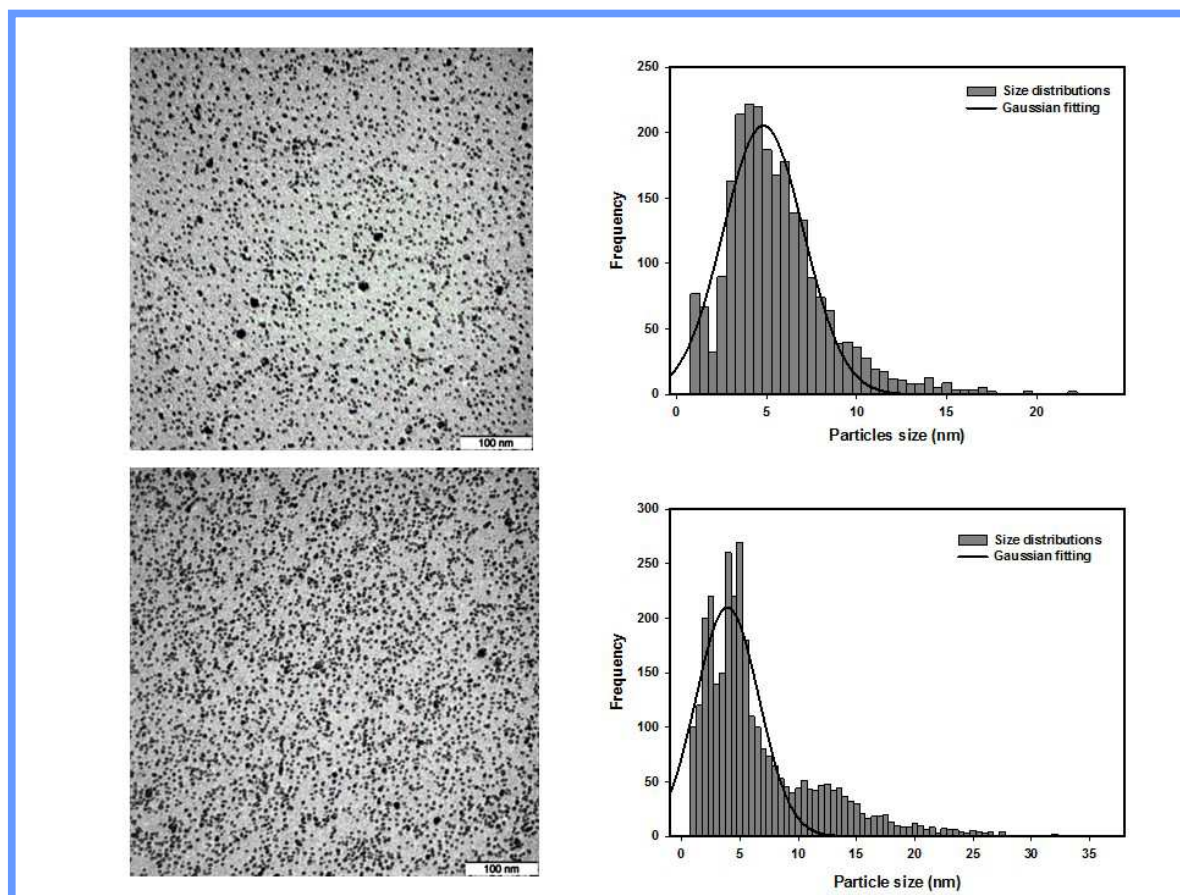


Figure 1(a) TEM images and **(b)** TEM size distribution and Gaussian fitting of monodispersed Pt nanoparticles irradiated at 80 kGy and 90 kGy. The average particle size is taken from the particle size distribution.

The sizes of Pt nanoparticles synthesized at different doses are shown in Figure 2. The figure demonstrates that the largest particle size is found for a dose of 80 kGy, and the smallest particle size at 120 kGy. There is a contest between the nucleation and growth processes in the formation of Pt nanoparticles. The general trend is that the average particle size decreases with increasing dose. At high doses, where the number of nucleation incidents is greater than the number of unreduced ions, the radiolytic reduction produces smaller particle sizes. At low doses, however, where the nucleation concentration is smaller than the concentration of unreduced ions, the zero-valent agglomerated atoms can be ionized by unreduced ions and subsequently reduced through hydrate electrons to create even larger Pt nanoparticles.

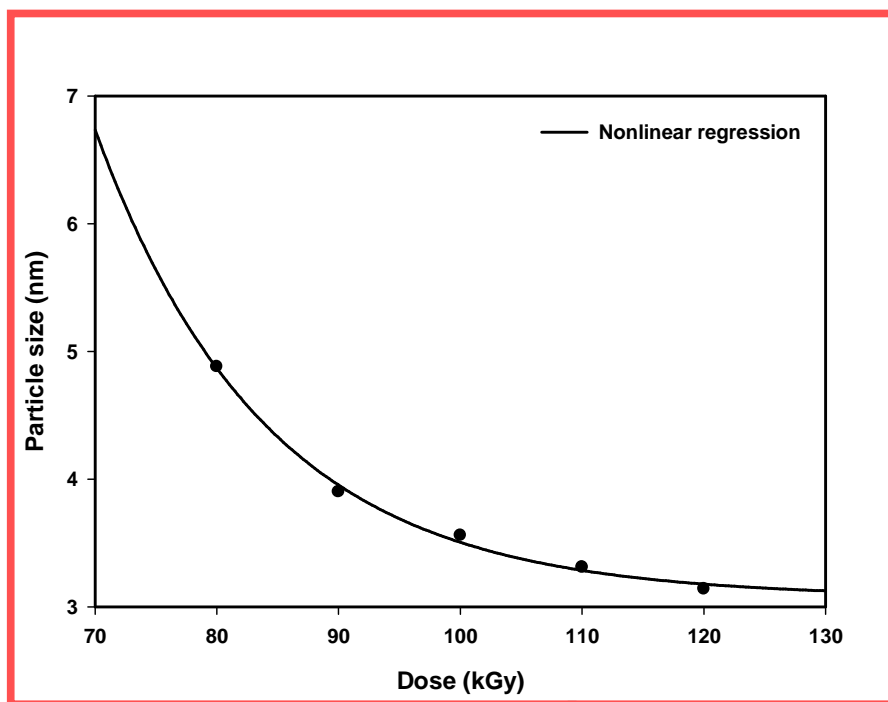


Figure 2. Average particle size of Pt nanoparticles versus gamma dose

3.3. Optical Properties

The evolution of the optical absorption spectra, with increasing gamma radiolysis dose, of Pt nanoparticles is presented in Figure 3. The results reveal two absorption peaks of Pt nanoparticles, which are (blue-) shifted to lower wavelength with increased dose, due to decrease of particle size. As the dose increased from 80 to 120 kGy the first absorption peak is blue shifted from 216 to 211.8 nm and the second peak from 264 to 259.8 nm, corresponding to decreasing particle size from 4.88 nm at 80 kGy to 3.14 nm at 120 kGy, as shown in Table 1.

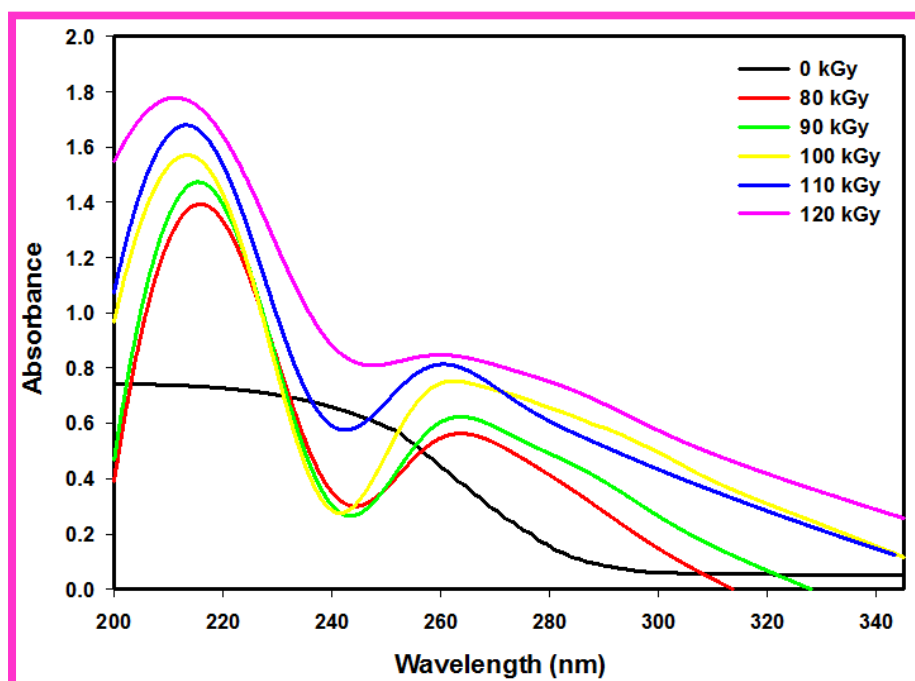


Figure 3. UV–visible absorption spectra of Pt nanoparticles synthesized at different gamma doses. The absorption maxima λ_{\max} blue shifted corresponding to decreasing particle size from 4.88 nm at 80 kGy to 3.14 nm at 120 kGy.

Table 1. Measured and calculated absorption maxima of Pt nanoparticles of particle size from 3.14 to 4.88 nm.

Dose (kGy)	Particle size (nm)	1 st absorption maxima $\lambda_{\max}(\text{nm})$		2 nd absorption maxima $\lambda_{\max}(\text{nm})$	
		Experiment	Theory	Experiment	Theory
80	4.88	216.0	216.63	264.0	264.91
90	3.90	215.0	215.38	263.0	263.56
100	3.56	213.9	213.92	261.6	262.10
110	3.31	212.8	212.05	260.8	261.36
120	3.14	211.8	211.54	259.8	259.85

The conduction band energy E of metal nanoparticles can be derived from the absorption maxima λ_{\max} according to $E = hc/\lambda_{\max}$, where h is Planck's constant, c the speed of light (Gharibshahi and Saion, 2010; Saion et al., 2013). The conduction band energy represents the amount of energy needed to excite the conduction electrons from the lowest energy state to the

higher-energy states observed in the UV-visible spectrometer measurements. Figure 4 and Figure 5 show the relationship between the conduction band energy and dose for the 216 and 264 nm absorption peaks, respectively. The absorption energy increases from 5.74 to 5.85 eV for the first peak and from 4.70 to 4.77 eV for the second peak with increasing dose from 80 to 120 kGy, due to the reduction in particle size from 4.88 to 3.14 nm. For smaller metal particles, with fewer metal atoms, the conduction electrons are less strongly attracted to the ionic cores, leading to a decrease in the absorption maxima or enlarge the conduction band of Pt nanoparticles.

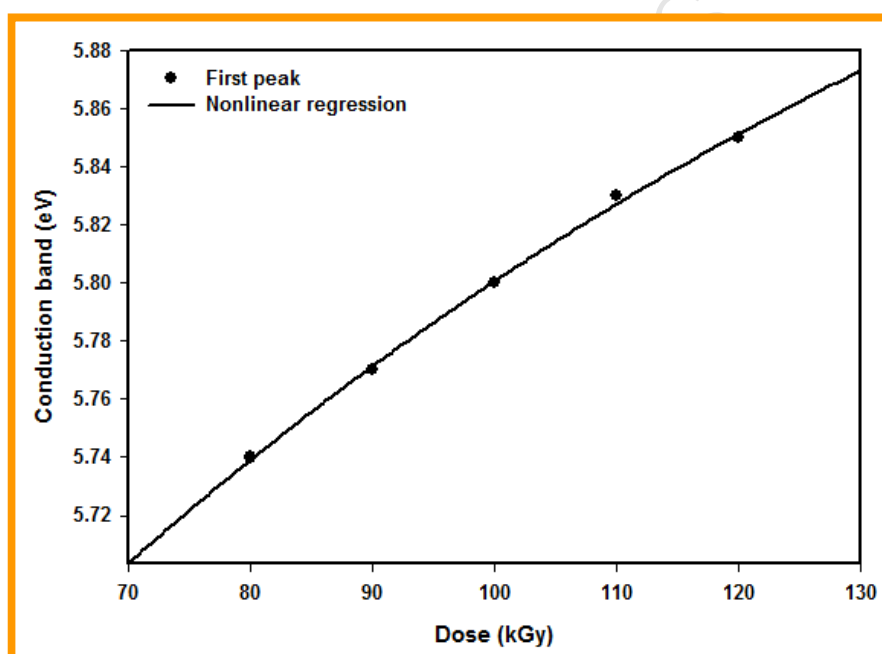


Figure 4. The first conduction band energy with the wavelength band 212-216 nm of Pt nanoparticles with increase of gamma dose from 80 to 120 kGy

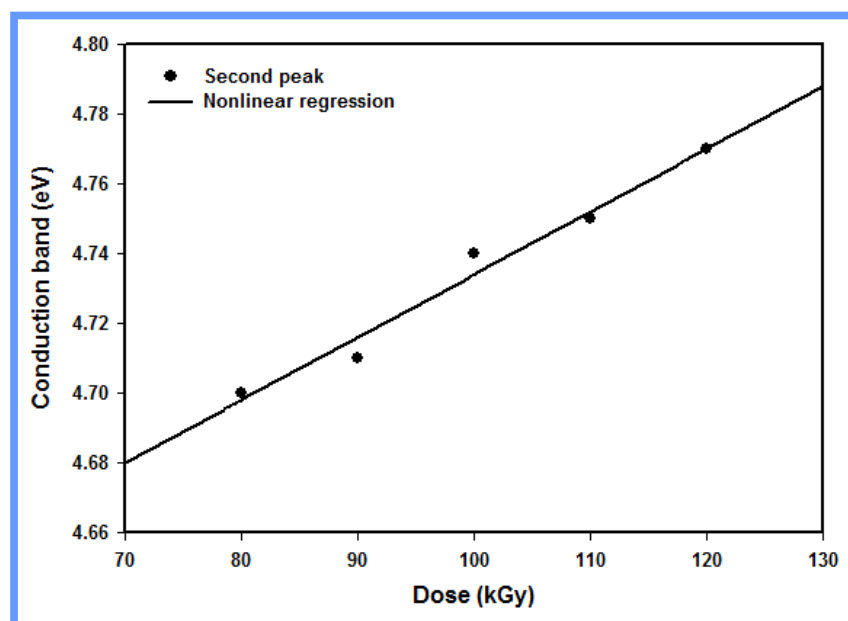


Figure 5. The second conduction band energy with the wavelength band 260-264 nm of Pt nanoparticles with increase of gamma dose from 80 to 120 kGy

The optical properties are vital for understanding the action of conduction electrons of metal nanoparticles and, to some extent, depend on physical parameters of the particles, such as particle size, crystalline structure, crystalline constant, number of conduction electrons and their quantum numbers. The theory of light absorption of metal nanoparticles is well documented and was first introduced by Gustav Mie in 1908 using classical electrodynamics. It is a non-quantum phenomenon, described as a coherent oscillation of conduction electrons on the surface of a metal–dielectric interface in resonance with the incoming electromagnetic waves, known as the localized surface plasmon resonance (LSPR) (Sherry et al., 2005; Willets and Van Duyne, 2007). However, the physical parameters mentioned above are not represented in the classical formulation. A more accurate theory of metal nanoparticles should consider a geometric structure built from the primitive unit cells of face-centered-cubic (f.c.c) lattice structure, the most common lattice structure of nanomaterials, and a correct electronic structure of metal nanoparticles based on the electronic structure of their atoms. From quantum physics principles, the optical absorption of metal nanoparticles like Pt nanoparticles may be described via intra-band excitations of conduction electrons from the lowest energy state to higher energy states.

The density functional theory of conduction electrons may be taken from the Thomas–Fermi–Dirac–Weizsacker atomic model that is fundamental for all ground state properties including absorption of metal nanoparticles. The Euler–Lagrangian equation $E[\rho(\mathbf{r})]$ of this model can be represented as

$$\frac{5}{3}C_k \int \rho(\mathbf{r})^{2/3} d\mathbf{r} + \frac{\eta}{8} \left[\frac{|\nabla \rho(\mathbf{r})|^2}{\rho^2(\mathbf{r})} - 2 \frac{\nabla^2 \rho(\mathbf{r})}{\rho(\mathbf{r})} \right] + v(r) + \int \frac{\rho(r')}{|r-r'|} dr' - \frac{4}{3}C_e \int \rho(\mathbf{r})^{1/3} d\mathbf{r} = E_0 \quad (2)$$

where, $\rho(\mathbf{r})$ is the density of conduction electrons of metal nanoparticle, E_0 is the Fermi energy, r is the displacement of conduction electrons from the center of the spherical nanoparticle, which is dependent on the Bohr radius a_0 , atomic number Z , and the principle, angular, and spin quantum numbers n , l , and, s , respectively. The first term of equation (2) is the Thomas–Fermi kinetic energy of the homogeneous free electron gas, with C_k being a constant. The second term is the Weizsacker correction to the Thomas–Fermi kinetic energy through inclusion of the exchange and correlation energy terms of inhomogeneous electron density, with η as a constant. The third term is the potential energy of the system. The fourth term is the classical Coulomb potential energy of electron–electron interactions. The last term is the non-classical exchange–correlation energy, including all the remaining quantum effects not captured by the kinetic energy; the classical Coulomb potential and C_e is the Thomas–Fermi–Dirac non-classical exchange–correlation energy constant. The relation between the density $\rho(\mathbf{r})$ and absorption $\sigma(\mathbf{r})$ may be written as $\rho(r) \approx (Z/\sigma(r))^{3/2}$, where Z is the atomic number. The transformation of energy density functional $E[\rho(r)]$ into absorption energy functional $E[\sigma(r)]$ can be achieved mathematically.

For this we have chosen an isolated Pt nanoparticle to have a solid pseudo-spherical structure, with f.c.c packing, a lattice constant of 0.393 nm and the electronic structure of the Pt nanoparticle according to the Jellium shell model; Pt(78)_N: (Xe)_N (5d⁹)_N(6s¹)_N, where N is the number of atoms made up the particle with the Fermi energy of 9.47 eV. Figure 6 shows the representation of the conduction electronic structure ($n=5$, $l=2$) and ($n=6$, $l=0$) of an isolated Pt nanoparticle. The optical absorption of the Pt nanoparticles are derived from intra-band excitations of conduction electrons from lower energy states of quantum numbers ($n = 5$, $l = 2$) and ($n = 6$, $l = 0$) to quantum number of higher energy states.

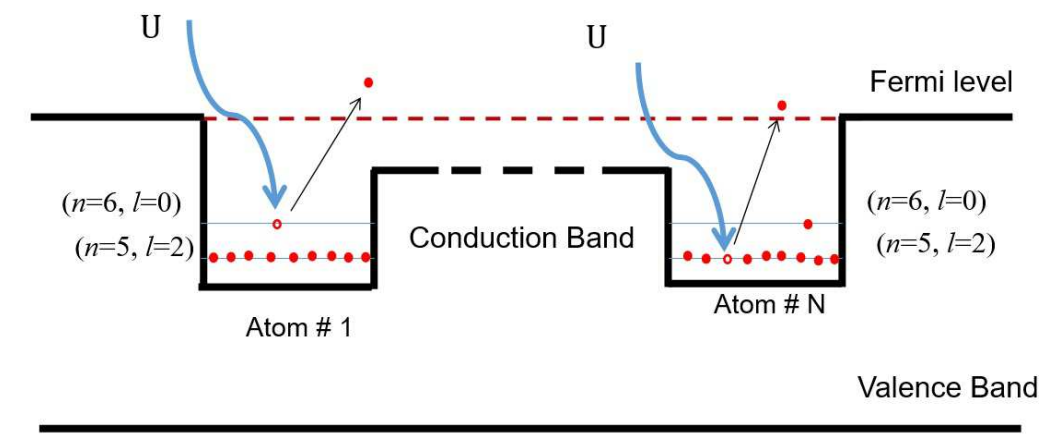


Figure 6. Representation of the conduction electronic structure of an isolated Pt nanoparticle

The calculated absorption spectra of Pt nanoparticles for diameters 4.88, 3.90, 3.56, 3.31, and 3.14 nm, modelling the measured absorption spectra of the same diameters obtained for doses of 80, 90, 100, 110, and 120 kGy respectively (Figure 3) are shown in Figure 7. Here, for each particle size, the calculated absorption spectra is represented by two possible intra-band excitations from lower-energy states ($n = 5, l = 2$) and ($n = 6, l = 0$) to higher-energy states ($n \geq 6; \Delta l = 0, \pm 1; \Delta s = 0, \pm 1$) and ($n \geq 7; \Delta l = 0; \Delta s = 0$) respectively, allowed by quantum mechanical selection rules. It is clear that the theoretical absorption spectra (Figure 7) and the experimental absorption spectra (Figure 3) are not similar in terms of the maximum intensity and the peak width. The reason is that the calculated spectra were based on an isolated single Pt nanoparticle of a given diameter, while the measured spectra were obtained from many synthesized Pt nanoparticles of different diameters. Figure 7 shows that, for the larger particle sizes, the number of atoms required to make up the particle is very large, so the number of conduction electrons used in the computation (much more than those of smaller particle sizes) leads to a significant increase in the maximum intensity and the width. The most important information on comparing the experimental and theoretical data is that the simulated absorption maxima, λ_{\max} agree very well with the measured values for all particle sizes, as shown in Table 1.

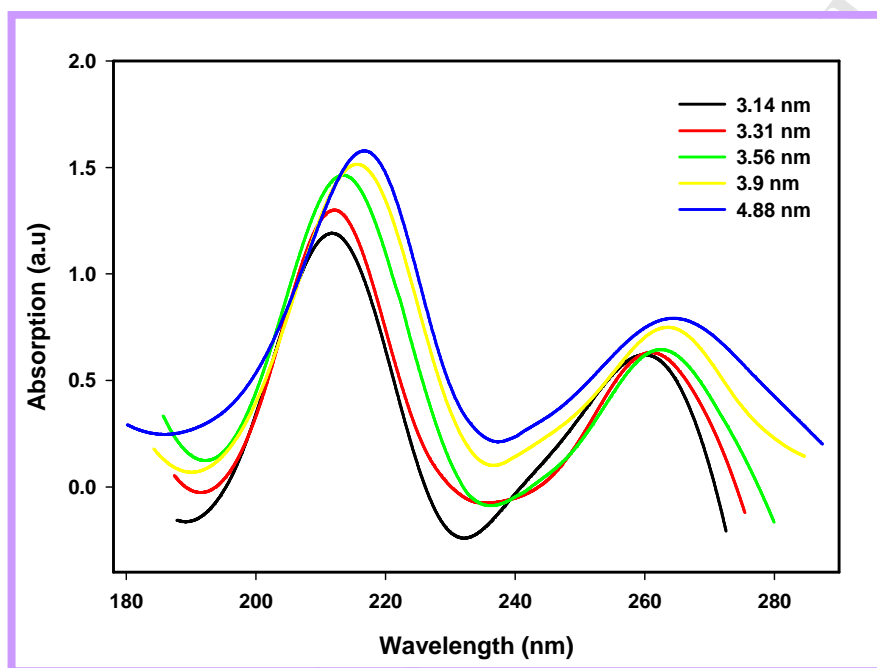


Figure 7. Theoretical absorption spectra of Pt nanoparticles at various diameters from 4.88 to 3.14 nm

The conduction band of the first and second absorption peaks of Pt nanoparticles are shown in Figure 8 and Figure 9. The figure show a decrease of experimental and theoretical nonlinear regression of conduction band data for increasing particle size, due to the quantum confinement effect of the conduction electrons of Pt nanoparticles. The experimental conduction band decreases from 5.85 to 5.74 eV for the first peak and from 4.77 to 4.70 eV for the second peak on increasing the particle size from 3.14 nm to 4.88 nm, as shown in Table 2. The theoretical conduction band curves decrease from 5.86 to 5.72 eV for the first peak and from 4.77 to 4.68 eV for the second peak on increasing particle size. Therefore, it is obvious that the conduction electrons have a significant impact on the optical properties of metal nanoparticles.

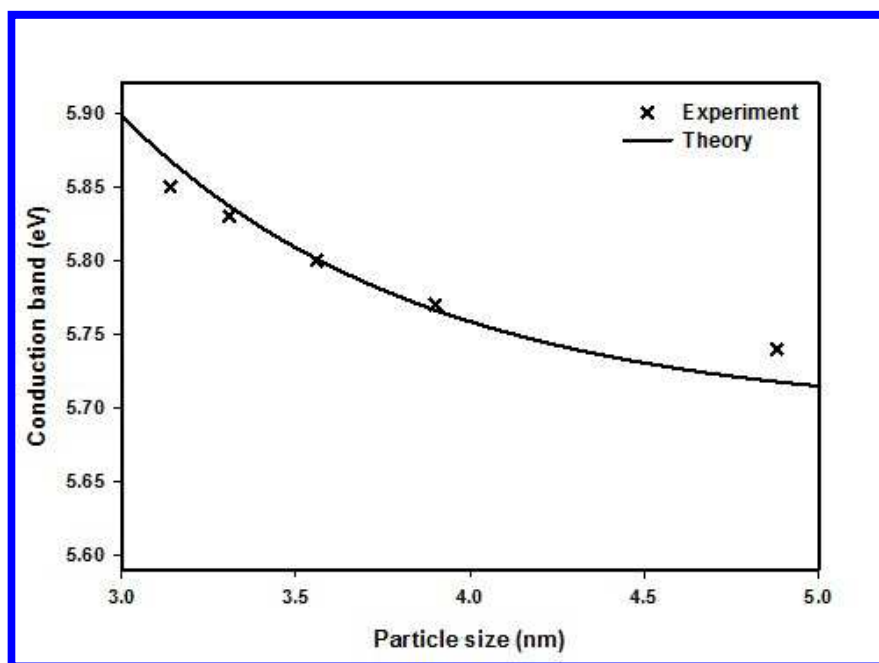


Figure 8. Conduction band of the first absorption peak with the wavelength band 212-217 nm of Pt nanoparticles

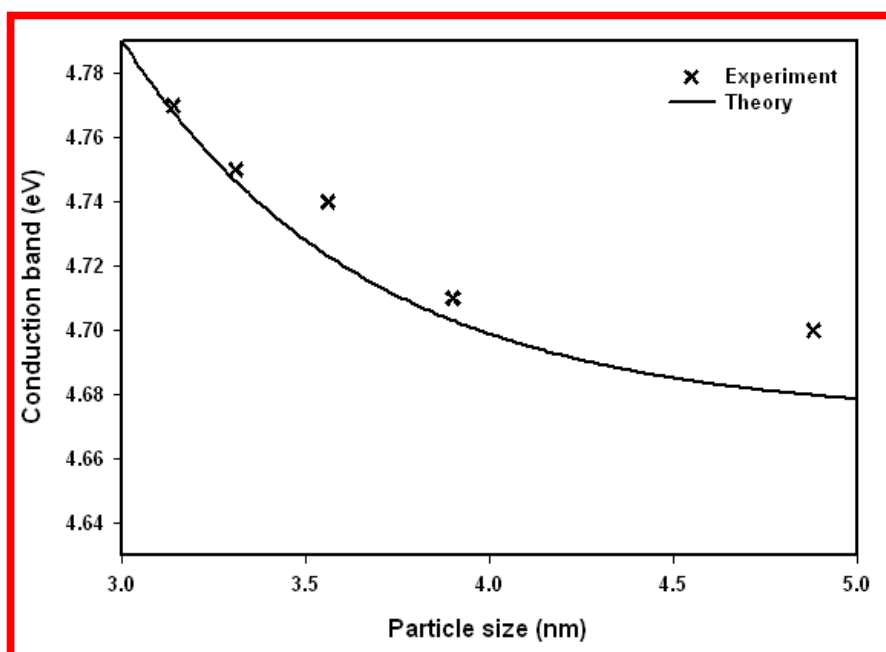


Figure 9. Conduction band of the second absorption peak with the wavelength band 260-265 nm of Pt nanoparticles

Table 2. Comparison between experimental and theoretical conduction bands of Pt nanoparticles synthesized at doses of 80 to 120 kGy.

Dose (kGy)	Particle size (nm)	1 st peak conduction band (eV)		Error (%)	2 nd peak conduction band (eV)		Error (%)
		Theory	Experiment		Theory	Experiment	
120	3.14	5.86	5.85	0.09	4.77	4.77	0.06
110	3.31	5.85	5.83	0.39	4.74	4.75	0.31
100	3.56	5.80	5.80	0.03	4.73	4.74	0.23
90	3.90	5.76	5.77	0.12	4.70	4.71	0.32
80	4.88	5.72	5.74	0.37	4.68	4.70	0.36

4. Conclusion

We successfully prepared platinum nanoparticles with diameters ranging from 4.88 to 3.14 nm by gamma radiolytic synthesis. The absorption spectra of platinum nanoparticles revealed two absorption maxima λ_{\max} at 216 and 264 nm, which are blue shifted toward lower wavelength as

the particle size decreases, corresponding to increasing the absorbed dose. Platinum nanoparticles possess two conduction bands with energies depending on particle size. This may give a new explanation for the strong catalytic activity of platinum nanoparticles. From our present understanding of Pt catalytic electronic structure, perhaps conduction electrons from both conduction bands could contribute to the catalytic action instead of conduction electrons from one conduction band for most metal catalysts. The optical absorption of platinum nanoparticles was discussed theoretically, based on intra-band excitations of conduction electrons from lower-energy states of quantum numbers ($n = 5, l = 2$) and ($n = 6, l = 0$) to higher-energy quantum numbers states allowed by quantum mechanical selection rules. We found that the calculated absorption maxima agree very well with the measured absorption maxima values. This work suggests that the theory of metal nanoparticles should be based on the intra-band quantum excitation of conduction electrons, which takes into considering the geometric and electronic structures of the metallic nanoparticles. The theory can be exploited for understanding the fundamental features of physical and chemical properties of other metallic nanoparticles, which are currently used in various fields of nanoscience and nanotechnology.

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Conflicts of Interest

The authors declare that they have no conflict of interest.

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Platinum nanoparticles were synthesized using gamma radiolytic technique. > The UV-visible absorption spectra were measured and revealed two steady absorption maxima. > The optical absorption simulated by using a quantum treatment. > The optical absorption of metal nanoparticles described by the intra-band quantum excitation of conduction electrons.